PREPARATION OF PPHMDSO THIN FILMS IN CAPACITIVELY COUPLED RF GLOW DISCHARGES UNDER DUSTY PLASMA CONDITIONS

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Abstract

The deposition of organosilicone thin films from mixture of hexamethyldisiloxane (HMDSO) and oxygen by using capacitively coupled R.F. glow discharges under dusty plasma conditions was investigated. High resolution topography and mechanical property maps of the prepared films were acquired by using atomic force microscopy techniques. The chemical bond and composition of the deposited films were analyzed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The mechanical properties of the films were studied using quasistatic as well as dynamic nanoindentation tests and their surface free energies were evaluated by means of contact angle measuring technique using several testing liquids exhibiting various surface tensions. The thermal stability of the films was studied using thermal desorption spectroscopy. Neural network modelling was used to study the effect of plasma parameters on the hardness of ppHMDSO films.

Keywords: PECVD, hexamethyldisiloxane, oxygen, mechanical properties

1. INTRODUCTION

Dusty plasma or complex plasma is a partially ionized gas containing dust particles that acquiring an electric charge due to their interaction with the surrounding ions and electrons. The particles can be introduced externally, or they can grow directly in the reactor as a result of the reaction in the plasma volume or the reaction on the solid surface within the reactor [1]. Dusty plasmas have been known almost as long as the plasmas themselves. It is widespread in astrophysical situations like in cometary tails or in interstellar clouds.

At the beginning in applications, important requirement for the plasma was high purity and presence of dusty particles in the discharges was undesired. Interest in the dusty plasma increased significantly in the nineties due to their potential applications in many areas. Dusty plasma was reported for a wide range of applications. For example, to produce low-k dielectric layers for microelectronics [2], formation of barrier layers [3,4] or biomedical applications [5]. Dusty plasma can also be used as a diagnostic tool for investigating phenomena in discharges [6].

Many studies have been devoted to the silane-based RF discharges since the silane-based plasma is a promising for producing nanostructured silicon thin layers [7, 8]. Hexamethyldisiloxane (HMDSO) is widely used for this deposition mainly because of its highly organic character, chemical stability, non-toxicity and high vapor pressure at room temperature. Thin films with a wide range of mechanical properties can be produced from hard inorganic SiO_2-like to soft polymer-like $SiO_xC_yH_z$ films properties just varying the plasma conditions, such as changing the gas mixture ratio [9,12]. Depending on the films structure, surface can be hydrophilic as well as hydrophobic or even superhydrophobic [10].

2. EXPERIMENTAL

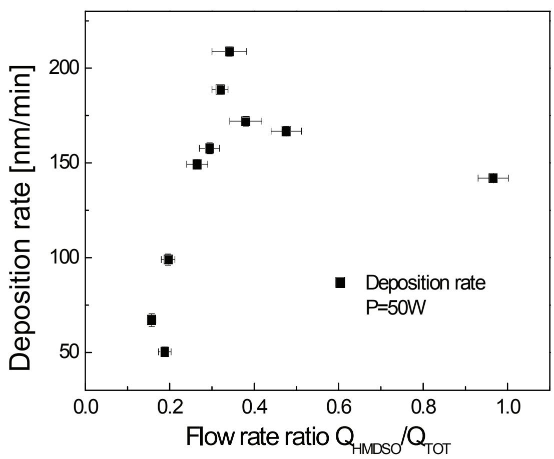
The studied films were deposited by PECVD from a mixture of HMDSO ($C_6H_{18}Si_2O$) and oxygen. The ratio of HMDSO flow rate Q_{HMDSO} and the total flow rate q ($q=Q_{HMDSO}/(Q_{HMDSO}+ Q_{O2})$) ranged from 0 to 0.95. The

HMDSO flow rate Q_{HMDSO} varied from 0 to 20 sccm, the oxygen flow rate Q_{O2} was varied from 3 to 11 sccm. The substrates were silicon wafers. The capacitively coupled plasma was generated in a parallel plate reactor using an r.f. generator working at frequency of 13.56 MHz. The applied power *P* varied from 25 to 75 W and the negative bias voltage ranged from -10 to -400 V.

The instrumented indentation technique was used to study the mechanical properties of the films. The samples were measured by means of Fischerscope H100XYp microindentor. The selected samples were measured on Hysitron TI 950 nanoindentor equipped with a sharp Berkovich diamond indenter. The indenter diameter was less than 50 nm. The morphology of the film surface and the indentation prints were studied using atomic force microscope Ntegra Prima NT-MDT.

3. RESULTS AND DISCUSSION

A large number of depositions were carried out in a wide range of deposition conditions as a continuation of our previous work presented in [12]. In **Figure 1** on the left there is a graph illustrating the dependence of the deposition rate on the ratio of HMDSO flow rate and the total gas flow rate for the 50W applied power. It can be seen that increasing the flow rate of HMDSO the rate of the deposition increases approximately up to the flow rate ratio of 0.35, then the deposition rate increase stopped and became almost independent on the flow rate ratio q. This fact is related to the start of the formation of dust particles in the plasma volume.



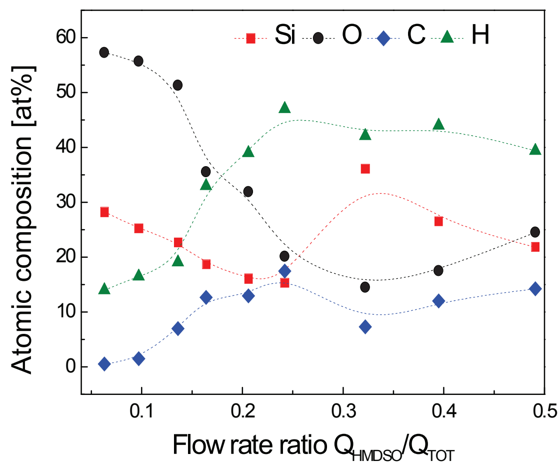


Figure 1 Dependence of the deposition rate on the flow rate ratio for applied power of 50 W (on the left). Dependence of the film atomic composition on the flow rate ratio (on the right)

Hardness and elastic modulus of the films are complicated functions of plasma parameters such as the applied power P, negative self bias voltage U_b and HMDSO to total flow rate ratio q as it is shown in **Figure 2**. In the recent work we focused on the samples from the region of dusty plasma deposition conditions. The deposition conditions for the selected samples are shown in **Table 1.**

Table 1 Summary of the deposition conditions for selected samples. Q_{O2} is the oxygen flow rate, Q_{HMDSO} is the HMDSO flow rate, *P* is the applied power, U_b is the corresponding negative bias voltage, *p* is the deposition pressure. The deposition time was 60 minutes.

Sample	Q_{O2} [sccm]	Q_{HMDSO} [sccm]	*P* [W]	U_b [V]	*p* [Pa]	*t* [µm]
VI215	5.2	2	25	-100	37	2.3±0.1
VI216	10	3.5	50	-90	53	3.1±0.1

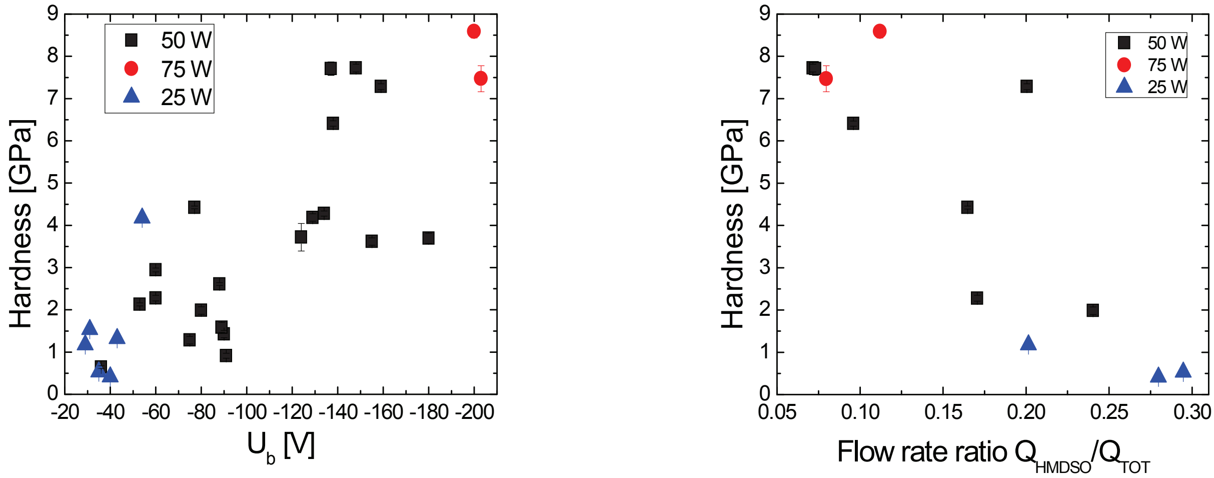


Figure 2 Hardness dependence of prepared films on the DC bias voltage U_b (on the left) and hardness dependence on the flow rate ratio q (on the right) for three different applied powers of 25, 50 and 75 W

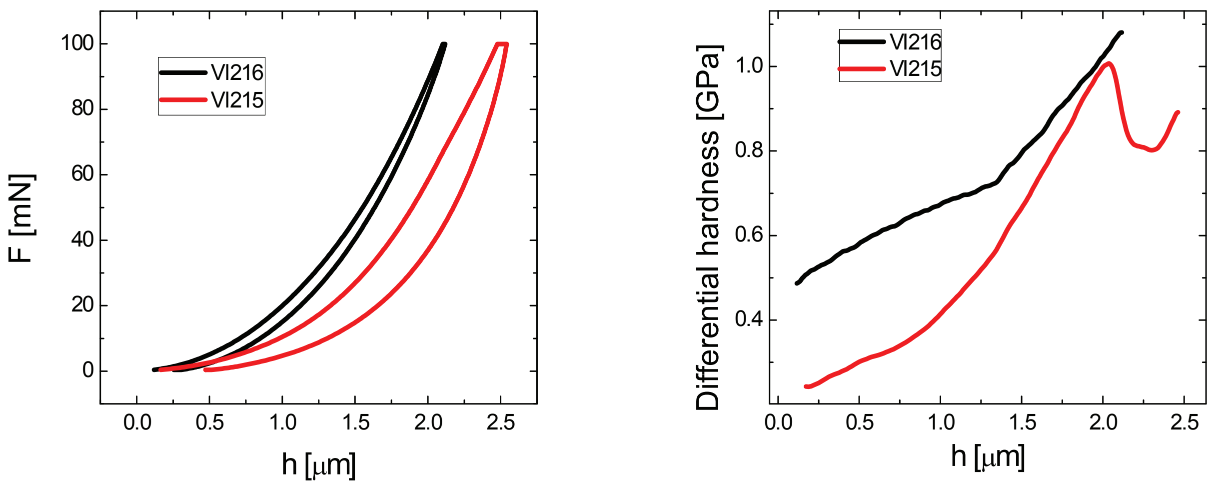


Figure 3 Loading/unloading curves (on the left) and examples of differential hardness dependence on the indentation depth h. The differential hardness was calculated as the derivative of the load function with respect to the increasing contact area

The films prepared under dusty plasma conditions are very elastic, even at maximum indentation depths reaching the film/substrate interface the plastic deformation of the film negligible as it is shown in **Figure 3** on the left. The differential hardness dependences prove the large resistance of the films against delamination or cracking. The jump on the differential hardness curve observed at around 2 μm for sample VI215 is related to the film/substrate interface. The composite character of the film VI215 is shown in **Figure 4**, where an example of AFM image of the sample surface acquired in semicontact mode is shown together with the magnitude and phase images. The maps of the stiffness and the work of adhesion were carried out from the analysis of the force-distance curves.

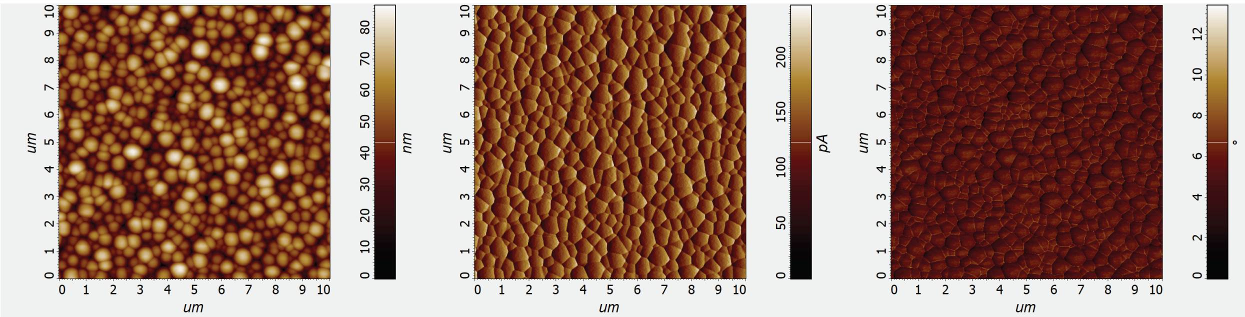


Figure 4 Topography image (on the left), magnitude (in the middle) and phase (on the right) for sample VI215

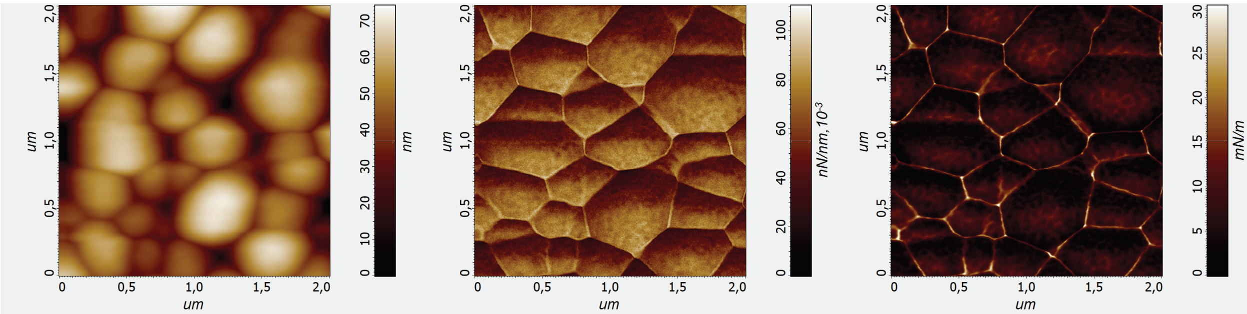


Figure 5 Topography image (on the left), mapping of the stiffness (in the middle) and work of the adhesion map (on the right) for sample VI215

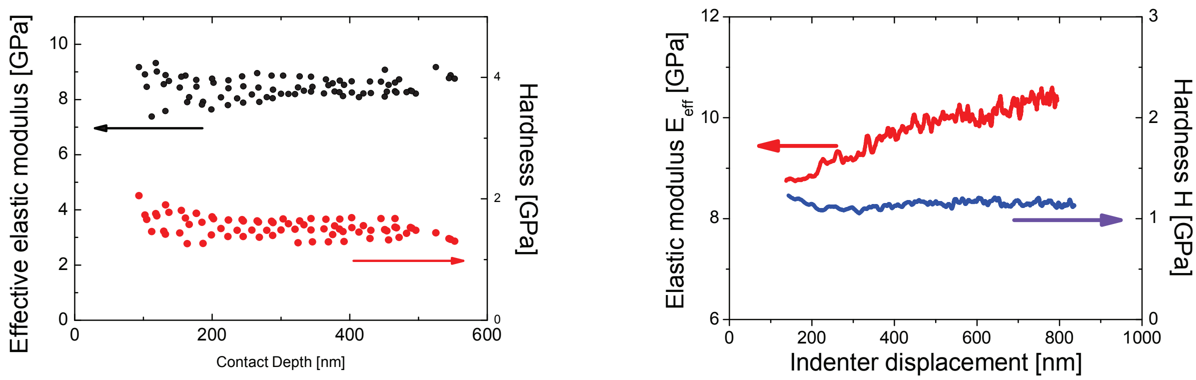


Figure 6 Hardness and effective elastic modulus profiles obtained at several different places on the sample VI126 using quasitatic nanoindentation tests with 20 unloading segments (on the left) and nanodynamic analysis using oscillating load with frequency of 200Hz and load amplitude in the range from 1 to 10 μN

Examples of hardness and elastic modulus profiles obtained from nanoindentation measurements on sample VI216 are shown in **Figure 6**.

4. CONCLUSION

Organosilicon plasma polymer films were prepared under dusty plasma conditions at relatively high deposition rates. The deposited films exhibited properties prospective for wide variety of applications, i.e. good adherence to silicon, glass and polymer substrates, good transparency to visible radiation, good thermomechanical stability, high resistance against aging at ambient environment, high elasticity and excellent fracture toughness. The nanocomposite character of the films was proven using atomic force microscopy techniques.

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